Old Dominion University Research Foundation ,

August 11, 1999

William P. Chu
Technical Officer
NASA Langley Research Center
Mail Stop 475
Hampton, VA 23681-0001

Reference: **Final Report-NASA Research Grant NAG-1-1869 (ODURF 170251)**
Research Title: *Measurement of Oxygen A Band Line Parameters by*
Using Modulation Spectroscopy with Higher Harmonic Detection

Dear Mr. Chu:

Enclosed please find a copy of the above referenced final report for the period ending
March 16, 1999. This project was under the direction of Dr. Amin Dharamsi, Principal
Investigator.

It is our hope that the enclosed journal publications entitled "Investigation of Interference
Between Absorption Lines by Wavelength Modulation Spectroscopy," "Reduction of
Effects of Fabry-Perot Fringing in Wavelength Modulation Experiments," and "Laser
Diode and LED Applications III" submission constitutes full satisfaction of the reporting
requirements under this grant. If this is not the case, we ask that you advise us at your
earliest convenience.

If your have any questions or need anything further please do not hesitate to contact me at
757-683-4293 extension 615.

Sincerely,

Linda K. Clarke
Grants and Contracts Administrator

Enclosure: Journal Publications – *Investigation of Interference between Absorption*
Lines by Wavelength Modulation Spectroscopy, Reduction of Effects of Fabry-Perot
Fringing in Wavelength Modulation Experiments & Laser Diode and LED
Applications III

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Investigation of interference between absorption lines by wavelength modulation spectroscopy

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Wavelength modulation spectroscopy is used to demonstrate that extremely weak absorption lines can be measured even when these lines suffer from interference from the wings of adjacent stronger lines. It is shown that the use of detection at several harmonics allows such interference to be examined clearly and conveniently. The results of experimental measurements on a weak magnetic dipole driven, spin-forbidden line in the oxygen A band, which experiences interference from the wings of a pair of adjacent lines towards the blue and red regions of line center, are presented. A comparison of the experimental results to theory is given. © *1998 American Institute of Physics.* [S0021-8979(98)06424-X]

Wavelength modulation spectroscopy has been used to perform measurements of weak absorption lines.[1-3] In such experiments a single mode laser is frequency modulated and swept over a single rotational line, followed by phase sensitive detection. Measurements have most often been performed with second harmonic detection. When the modulation frequency is small, the effective result is that the probe samples the absorption line shape with the laser carrier and its side bands. As the absorption profile is swept, one obtains signals that have a structure that resembles (but is not identical to) the derivative of the line shape function. For example, second harmonic detection, an area where most of the work has been done in the past, gives signals that have features analogous to the second derivative of the profile.

Recently we have extended the use of wavelength modulation spectroscopy by using higher harmonic detection.[4-6] It has been shown that, while the signal magnitude decreases with the detection harmonic order, the signal to noise ratio can increase up to an optimum harmonic order, N_{opt}, whose value depends on the complete experimental noise spectrum. The main result of higher harmonic detection experiments is that there are many situations in which it is advantageous to work with detection orders greater than the commonly used second harmonic.

We present experimental and theoretical results that show that a set of wavelength modulation experiments using detection at several harmonics of the fundamental can clearly resolve very weak lines even if such weak lines suffer from interference by the wings of adjacent stronger lines. Such interference from wings of adjacent lines is clearly identifiable by using the results of a set of experiments employing detection harmonic orders of one, two, and three.

The experimental apparatus used has been described previously.[4-6] Several absorption lines in the oxygen A band were measured in open atmosphere in a multipass cell that was assembled using the design of Altmann *et al.*[7] This configuration was chosen because it most closely reproduces the

conditions existing in applications of interest to us. Such applications include the measurement of atmospheric constituents by solar and lunar occultation, as well as with remotely located laser sources. The results shown in Fig. 1 are those obtained for the weak oxygen RQ (31,32) line with an absorption cross section of 5.06×10^{-26} cm^2 cm^{-1} molecule^{-1}.[8] Experimental and theoretical results are shown for first, second, and third harmonic detection.

Figure 2 shows details of the calculated signal. It is to be noted that the RQ (31,32) line is sandwiched between two stronger lines: the RQ (25,26) line towards the red side of line center, and the RQ (27,28) line towards the blue side. These lines have line strengths of 4.436×10^{-25} and 2.284×10^{-25} cm^2 cm^{-1} molecule^{-1}, respectively.[8] In order to obtain the match between theory and experiment shown in Fig. 1, it was necessary to include the effects of these two lines which, while in absolute terms are quite weak, are nonetheless several (8.8 and 4.5) times stronger than the RQ (31,32) line itself. According to the HITRAN '96 database[8] there are four additional, but much weaker, transitions between the RQ (25,26) and the RQ (31,32) lines. These additional lines are the following: RQ (30,31), 2.0340×10^{-28} cm^2 cm^{-1} molecule^{-1}; RQ (27,28), 5.763×10^{-28} cm^2 cm^{-1} molecule^{-1}; RQ (29,30), 2.9200×10^{-28} cm^2 cm^{-1} molecule^{-1}; RQ (28,29), 4.1310×10^{-28} cm^2 cm^{-1} molecule^{-1}. Computations of the expected signals were made with the contributions of all the seven lines mentioned above included. It was found that the contributions of the last four lines given above, which are weaker by several orders of magnitude compared to the RQ (31,32), RQ (25,26), and RQ (27,28) lines, were negligible. In addition, a search of the HITRAN'96 database indicates that there are no absorption lines from other species such as water vapor or common pollutants in the atmosphere in this region of the spectrum. For convenience and for the sake of clarity, therefore, Fig. 2 shows only the total signal calculated as the result of interaction of the RQ (31,32), RQ (25,26), and RQ (27,28) lines.

Note that while the agreement between theoretical and experimental results shown in Fig. 2 is very good, it is not perfect. The relatively small discrepancies between theory

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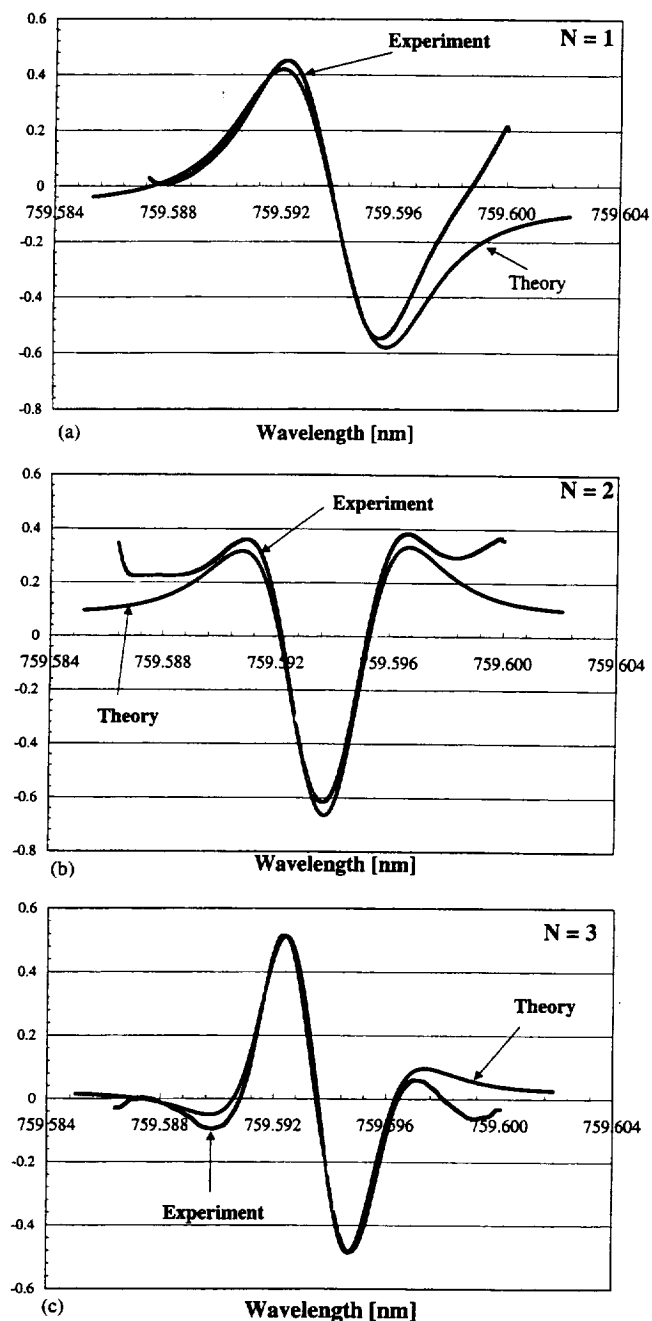[a])Electronic mail: dharamsi@ece.odu.edu

FIG. 3. Comparison between experimental and theoretical results calculated by assuming that only the RQ (31,32) line contributes to the signal. A comparison between Figs. 3 and 1 shows clearly that the contributions of the wings of the adjacent RQ (27,28) and RQ (25,26) lines need to be accounted for in order to get good agreement between theory and experiment. (a) First harmonic detection signal; (b) second harmonic detection signal; (c) third harmonic detection signal.

described here would not suffer from such a limitation and, since the contributions of the individual overlapping lines can be obtained easily, one would be able to obtain information of both species.

The method also has applications in investigating the wings of absorption lines from which information on the dynamics of molecular collision can be obtained. For instance, it is known that Dicke narrowing of lines influences not only the central part of an absorption line, but it also modifies the profile in the wings.[12-14] This line narrowing occurs, under certain conditions, with increasing pressure essentially because the translational degree of freedom is constrained by molecular collisions. When the optical wavelength is on the order of the mean free path, a quasicoherent process leads to the line center region being narrowed. Simultaneously, the wing structure is modified and hence details of line overlap are affected. These wing structures and the consequent overlapping of lines can be studied conveniently by modulation spectroscopy using several harmonic detection orders.

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Reduction of effects of Fabry–Perot fringing in wavelength modulation experiments

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One of the factors limiting the sensitivity of wavelength modulation experiments is the fringing that is created by inadvertent multiple reflections between parallel optical surfaces in the apparatus. It is shown that the effects of this "étaloning" can be countered by using detection harmonic orders greater than the second. A theoretical basis for the effect is presented and compared with experimental results obtained. © *1998 American Institute of Physics.* [S0003-6951(98)02124-X]

Wavelength modulation experiments, performed by many researchers, have provided sensitive measurements of concentrations, temperatures, and velocities of gaseous species.[1,2] In such experiments, one imposes a low frequency modulation on the incident single-mode laser beam that probes the target species. The signal is detected by a photodetector and processed by a lock-in amplifier set to demodulate at the modulation frequency, or at one of the harmonics of this fundamental frequency. One then generally obtains an increased signal-to-noise ratio compared to experiments utilizing "direct absorption," i.e., those not utilizing the principles of frequency modulation coupled with phase-sensitive detection.

A large amount of work has been performed using second-harmonic detection, where the detected signal is demodulated at the second harmonic of the modulation frequency. Some work has also been done with higher harmonic detection.[3–6] It has been shown that there are some distinct advantages in going to such higher harmonic detection, including an increased sensitivity to density fluctuations and a better resolution in congested spectra.

In all these experiments one always has to contend with the usual sources of noise including that originating in the laser, the photodetector, and the detector electronics. However, an additional source of noise that is of particular importance in modulation spectroscopy is due to "Fabry–Perot étaloning." This oscillatory noise signal appears because of undesired multiple reflections between parallel surfaces, formed by optical components in the apparatus. In many experiments, this limits the signal-to-noise ratio. The problem is often exacerbated in experiments that incorporate multipass cells, where overlapping between optical beams at the mirror surfaces maybe difficult to avoid.

Several experimental techniques involving asynchronous jittering have been used to reduce the deleterious effects of such fringing. One method involves the introduction of an asynchronous current in addition to the usual modulation current through the diode laser.[7] Another method uses optoacoustic asynchronous jittering of the offending optical component.[2] In both cases, étaloning is reduced because the measurement is performed over an integrating time constant that is many times longer than the inverse of the fringe period.

We examine the effects of noise due to Fabry–Perot étaloning in wavelength modulation experiments. In particular

the effects of detection at various harmonics are examined. It is shown that there are conditions under which the experimental signal-to-noise ratio (where the noise is the Fabry–Perot étaloning signal) can be increased substantially by increasing the harmonic detection order. A simple analysis is presented, followed by some experimental results that illustrate the utility of the method of higher harmonic detection.

An important parameter in the experiments discussed here is the ratio of the Q factors of the parasitic étalon and the line being monitored. Qualitatively, the results obtained can be explained by recognizing that wavelength modulation experiments yield signals whose functional form can be approximately described by the frequency derivative of the appropriate lineshape function. While in any real experiment the signals differ from derivatives because of the necessarily finite values of modulation indices that must be used, the qualitative nature of the derivatives is preserved even for relatively large modulation indices.[4] Hence, if the quality factor of the absorption profile being measured is larger than that of the étalon, an increased effective signal-to-noise ratio can be obtained with increasing harmonic order. This is because corresponding frequency derivatives of a high-Q transmission function are greater than those of a low-Q feature. The parasitic Fabry–Perot étalon that occurs often is the result of reflectivity ($<4\%$) at uncoated interfaces and it can have a Q factor that is smaller than that of the absorption feature being monitored. Higher harmonic detection is then advantageous.

An approximate expression for a wavelength modulation signal is[3]

$$S^N \approx I_0 L \frac{2^{-N}}{N!} \beta^N \frac{\partial^N[\alpha(\nu)]}{\partial \nu^N}, \tag{1}$$

where I_0 is the incident intensity, L is the absorption path length, β is the frequency modulation amplitude, N is the harmonic detection order, and α is the absorption coefficient.
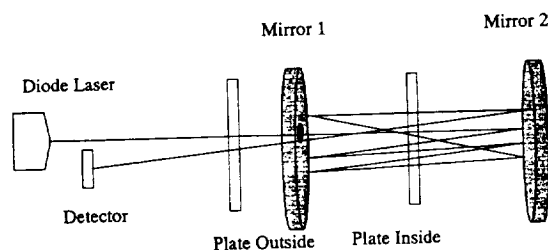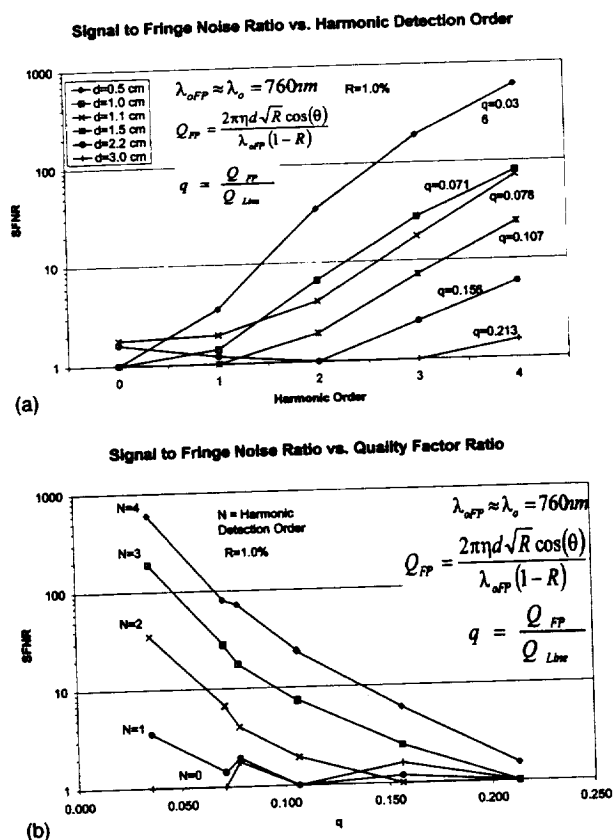

FIG. 1. Multipass cell arrangement.

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Signal to Fringe Noise Ratio vs. Harmonic Detection Order

(a)

Signal to Fringe Noise Ratio vs. Quality Factor Ratio

(b)

FIG. 3. (a) Improvement in signal-to-fringe-noise ratio with increasing detection harmonic order for various values of quality factor ratio, q. (b) Decrease in signal-to-fringe-noise ratio with increasing values of quality factor ratio, q, at fixed detection harmonic orders.

The computed signals were obtained by using a calculation based on the method of Wilson[9] which was extended to incorporate effects of residual amplitude modulation that occurs simultaneously in a wavelength modulation experiment using diode lasers. We also introduced a transmission function that accounts for the parasitic étaloning of the form given by the second term on the right hand side of Eq. (2) above. The values of ϕ_i were obtained by modeling the multipass cell with a ray-tracing program, and incorporated into the calculation.

The results shown in Fig. 2 are those obtained by monitoring the oxygen A-band RQ (15,16) rovibronic line at 760.093 nm. A Rautian–Sobelman line shape profile was used and the line parameters were taken from the work of Ritter and Wilkerson.[10] In Eq. (2) the absorption cross section $\sigma_{abs} = \overline{\sigma_{abs}} g(\nu)$, where $\overline{\sigma_{abs}}$ is the integrated absorption cross section and $g(\nu)$ is the line shape function.

The results in Fig. 2 show that with first-harmonic detection, the fringe is quite pronounced, but it decreases with second- and third-harmonic detection such that by third-harmonic detection, there is hardly any fringing at all. It is clearly seen that the signal to fringe-noise ratio (SFNR) decreases as the harmonic detection order increases.

A systematic investigation based on the ratio of the Q factors of the absorption line and the parasitic étalon was carried out. The Q factor of the étalon is

$$Q_{F-P} = \frac{2\pi}{\lambda_{0F-P}} \eta d \frac{\sqrt{R}}{(1-R)}$$

and that of the line is $Q_{Line} = \nu_0 / \Delta\nu$. It is seen from Fig. 3 that the ratio $q = Q_{F-P}/Q_{Line}$ plays an important role in determining whether or not the signal-to-noise ratio improves with increasing N.

Figure 3(a) shows results of calculations performed by using different parameters for the parasitic étalon. The SFNR was measured by taking the ratio of the signal magnitude to the fringe magnitude. The results displayed are those for values of reflectivity corresponding to uncoated surfaces used in our experiments. The value of the ratio q was varied by using various distances for the separation of the étalon surfaces. Q_{Line} was held fixed.

Figure 3(a) shows that increasing the harmonic detection order, N, generally results in an increase in the SFNR for the several different values of q explored. All these values of q are less than one, as expected. It is also seen that for a fixed harmonic detection order, the value of SFNR increases with decreasing q. Both these observations are consistent with the discussion above; namely, that higher harmonic detection would play a role in suppressing the effect of fringe noise when q is small. Figure 3(b), which is derived from Fig. 3(a), shows that the smaller q is the greater is the improvement of the SFNR, at a fixed detection harmonic order.

The results of this work show that detection at higher harmonics can lead to an improvement in the signal-to-fringe-noise ratio in wavelength modulation experiments where Fabry–Perot étaloning is a problem. While there are several different methods that have been used to reduce the effects of étaloning, the method discussed in this letter, seems to be the simplest. Hence for example, one does not need to mechanically jitter any optical element, as is done in some experiments.[2] There are obvious difficulties involved with experiments that involve such jittering that would be avoided by the method of higher harmonic detection. The derivative like features of wavelength modulation signals have been shown to lead to increased sensitivity to density fluctuations[3,4] as well as an increased resolution[5] of lines that are nearly overlapping. The results of the work outlined here show that, in addition to these other advantages, higher harmonic detection can also play a significant role in suppression of noise due to Fabry–Perot fringing.

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PROCEEDINGS

Laser Diode and LED Applications III

Kurt J. Linden
Chair/Editor

10–11 February 1997
San Jose, California

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Modulation Spectroscopy with Diode Lasers: Applications in Spectroscopy and Non-intrusive Measurements

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ABSTRACT

Theoretical and experimental results related to wavelength modulation absorption spectroscopy using single-mode diode lasers are presented. This method uses a phase-sensitive detection technique, and the implications of detection at harmonics greater than the commonly used second-harmonic are discussed. It is shown that several advantages accrue with such higher-harmonic detection. Applications of the method in increasing sensitivity to measurements of density and temperature fluctuations; in increasing wavelength resolution of modulation and pressure broadened congested spectra; and in applications for accurate characterization of absorption lines of molecular spectra, are discussed. It is shown that wing structure of absorption lines can be obtained with much more accuracy using higher harmonic detection than either direct absorption or the commonly used second harmonic detection technique. Experimental results obtained are compared to the predictions of the theory developed.

1. INTRODUCTION

Wavelength modulation spectroscopy is a well-known technique that has been used to perform non-intrusive measurements of many different types, including identification of gaseous species, the measurement of densities, temperatures and flow velocities. The availability of diode lasers has resulted in an apparatus that is light-weight, compact, fiber-optic compatible as well as inexpensive.

In such an experiment a single mode laser beam, tuned into the vicinity of the absorption feature being monitored, is incident upon the sample. The laser is frequency modulated and swept slowly across the absorption line. The signal is then detected with a lock-in amplifier. A feature that has often characterized such experiments in the past is that the detection was performed at the second harmonic of the modulation frequency. The improvement in the signal to noise ratio that results from modulation followed by phase sensitive detection is generally much higher than that obtained in direct absorption experiments.

In recent work we have shown [1-8] that there are many instances in which the use of detection harmonics greater than the second can be advantageous. For instance, it is possible, by use of harmonics greater than the second, to obtain a greater sensitivity to density fluctuations, as well as an increase in the resolution of adjacent and partially overlapping lines.

The basic reason for this is relatively easily explained: (when the modulation indices are small) a modulation experiment such as the one under discussion results in a signal that approximates the derivative (in the frequency domain) of the line shape function. In actual experiments one has to often use modulation indices that are relatively large but, even here, it can

be shown [3] that the signal retains its major derivative-like features. This results in signal characteristics that show the advantages mentioned above. For instance, it is relatively straightforward to show that the dependence of the signal on density fluctuations is given approximately by n^{-N}, where n is the density and N the harmonic detection order [4]. Similarly, small features in the absorption profile appear as relatively large changes in the derivatives of these profiles; hence, one obtains an increased resolution in the wavelength regime, enabling one to distinguish between features due to overlapping lines [2].

In this paper, we present the results of experiments that demonstrate many of these advantages. We also give a corresponding theoretical treatment that explains the experimental results obtained. The paper discusses the above applications that we have demonstrated, as well as potential future applications of the method of wavelength modulation spectroscopy, with particular attention to higher harmonic detection.

Another very useful application of wavelength modulation with higher harmonic detection is in investigating the wing structure of molecular absorption lines. Results of experiments demonstrating this are presented.

2. THEORETICAL AND EXPERIMENTAL RESULTS

It can be shown that the Nth harmonic detection signal can be written as:

$$S^N = -n\bar{\sigma}LI_0 \, (-1)^{\frac{[N]}{2}} \sum_{v=0}^{\infty} \left(\frac{\beta}{2}\right)^{2v+N} \frac{1}{v!(v+N)!} \, g^{2v+N}(v) \qquad (1)$$

In this equation [N] = N for even values of N, [N] = N-1 for odd values of N, n is the density of the absorbing species, $\bar{\sigma}$, is the integrated absorption cross section, v is an integer, $g^{2v+N}(v)$ is the (2v + N)th derivative of the lineshape function, and L is the optical path length in the absorbing medium. In the limit of a small modulation index, the v = 0 term dominates and one obtains a signal that is proportional to the Nth derivative of the lineshape function of the absorbing feature. Therefore, the v = 0 term leads to derivative spectroscopy.

One can extend this result to include effects of simultaneous amplitude modulation such as would be present in an experiment using a diode laser. Hence, we write the electric field intensity of the single mode laser beam as:

$$E(t) = E_0\left\{1 + \frac{r}{2} \, Sin(\omega_m t + \psi\,)\right\} \left\{Cos(2\pi\bar{\nu}_L t + \beta \, Sin\omega_m t)\right\} \qquad (2)$$

Here, β (in Hz) is the magnitude of the frequency modulation, r is the dimensionless magnitude of the amplitude modulation, and ψ is the phase difference between the amplitude and wavelength modulation components.

This method yields a result for the signal which is a sum of eight terms, five of which lead to infinite series that involve the weighted derivatives of the lineshape function. These functions

are given explicitly in reference [3]. In the work described in this paper, we assume that the absorption lineshape function has a Voigt profile and use the expressions we have derived previously for the derivatives of the Voigt lineshape function.

An important application of higher harmonic detection which has not been recognized so far is that such experiments allow one to examine the wing structure (see Figs. 1 and 2) of lines in much more detail than would be possible with direct absorption or with detection at the usual second harmonic.

For convenience, the other characteristics of modulation spectroscopy with phase-sensitive detection, at higher harmonic order, which have been studied in our previous work are summarized here. These characteristics are (i) increased sensitivity to density and temperature fluctuations, (ii) increased resolution of overlapping lines.

A characteristic of wavelength modulation with detection at Nth harmonic has been shown to be a dependence of the signal magnitude with density that is approximately linear initially, but which follows, approximately, an n^{-N} dependence, for densities greater than $n_{\delta,N}$. These values of density ($n_{\delta,N}$) are those at which the signal magnitudes at linecenter, attain their peak values.

The region $0 < n < n_{\delta,N}$ defines the effective Doppler broadened regime. The range of the latter (i.e. the value of $n_{\delta,N}$) depends on the order, N, of the detection harmonic and the values of the modulation indices. This description encompasses the well-known behavior of signal magnitude at line center when direct absorption is used where it is found that [9], in the collision broadened regime, the signal magnitude at linecenter stays approximately constant (corresponding to an n^{-N-0} dependence). The general characteristic of modulation spectroscopy (the dependence of the signal magnitude approximately as n^{-N} in the collision broadened regime) with any harmonic detection may be exploited in obtaining measurements of density fluctuations that are more sensitive for larger N than smaller ones [4]. This is shown in Fig. 3 where $b_{\delta,N}$ denotes the collision broadening parameter associated with the density $n_{\delta,N}$.

Modulation spectroscopy allows better resolution of spectra that may be congested either because of transition energy level coincidences and/or broadening by whatever mechanism (for example collision broadening, or modulation broadening) available. This is seen in Fig. 4.

3. DISCUSSION

It is seen from the results presented above that when one uses higher harmonic detection there are several advantages that can be obtained. These advantages are obtained in spite of the fact that the magnitude of the signal with higher harmonic detection is smaller than that at lower harmonics. (This fact, however, ultimately is responsible for the existence of an optimal value for harmonic detection that applies to a particular experiment.) The characteristics and advantages of higher harmonic detection, depicted in the results given above, and discussed below, can be understood from the fact that the signal, using Nth harmonic detection, incorporates many of the features of the derivatives of the line shape function; i.e., at minimum, the Nth harmonic signal exhibits characteristics that originate from those of the derivatives of the line shape function.

3(a)   **Wing structure of lineshape function and collision cross-sections.** Wavelength modulation with higher harmonic detection is well-suited for the study of the lineshape function of an absorption line in the wings. The reason for this is clear since any minor variations of the line
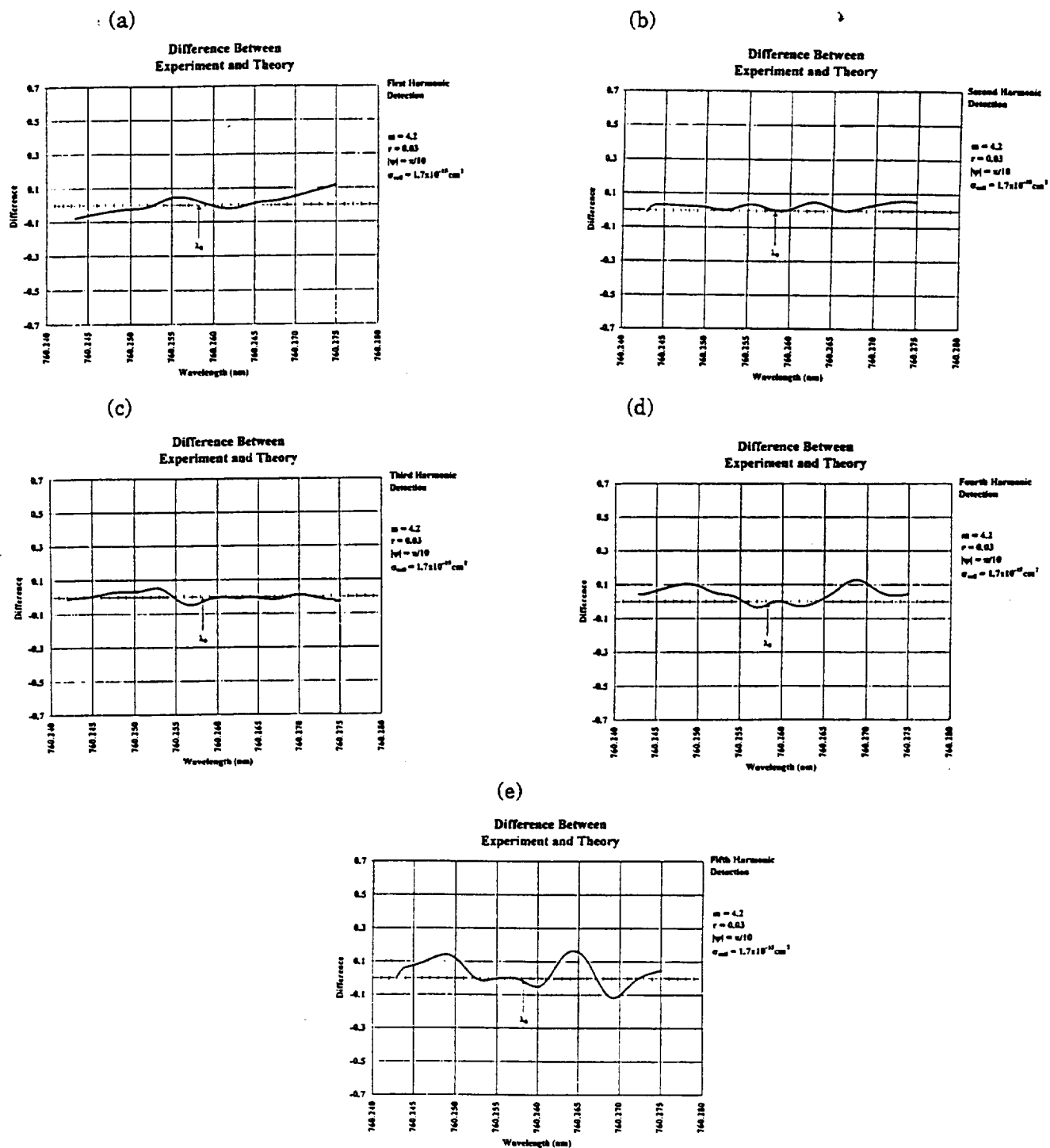
(a)

**Difference Between
Experiment and Theory**

First Harmonic
Detection

m = 4.2
r = 0.83
|ν| = u/10
σ_ext = 1.7×10⁻¹⁰ cm²

(b)

**Difference Between
Experiment and Theory**

Second Harmonic
Detection

m = 4.2
r = 0.83
|ν| = u/10
σ_ext = 1.7×10⁻¹⁰ cm²

(c)

**Difference Between
Experiment and Theory**

Third Harmonic
Detection

m = 4.2
r = 0.83
|ν| = u/10
σ_ext = 1.7×10⁻¹⁰ cm²

(d)

**Difference Between
Experiment and Theory**

Fourth Harmonic
Detection

m = 4.2
r = 0.83
|ν| = u/10
σ_ext = 1.7×10⁻¹⁰ cm²

(e)

**Difference Between
Experiment and Theory**

Fifth Harmonic
Detection

m = 4.2
r = 0.83
|ν| = u/10
σ_ext = 1.7×10⁻¹⁰ cm²

Fig. 2. The differences between theoretical and experimental results

Fig. 1. Comparison between theoretical and experimental results

(a)

Difference Between Experiment and Theory

(b)

Difference Between Experiment and Theory

(c)

Difference Between Experiment and Theory

(d)

Difference Between Experiment and Theory
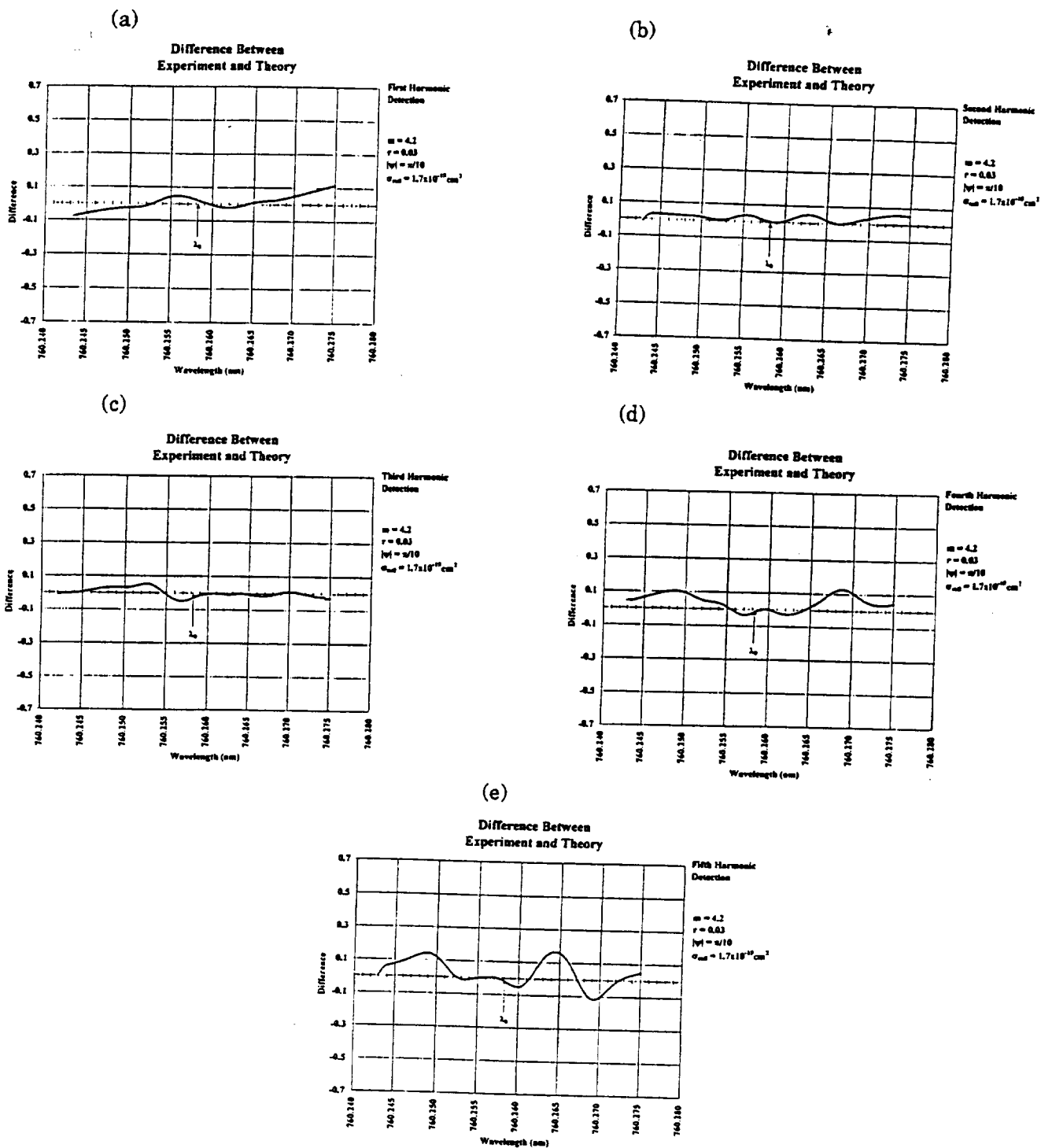
(e)

Difference Between Experiment and Theory

Fig. 2. The differences between theoretical and experimental results

shape function (for example in a direct absorption signal) from a "standard" line shape function, such as the Voigt function, for instance, will generally be more obvious when the derivatives (of the signal expected from the standard function and the signal obtained experimentally) are compared. In addition, generally speaking, the greater the derivative order the greater is this difference. (It is of course clear that, as mentioned above, the signal with Nth harmonic detection only approximates the Nth derivative signal.)

The experimental results shown in Figs. 1 and 2 show this very clearly. For example, Fig. 1(e) shows that there is a significant discrepancy in the wings when one compares the experimental signal with fifth harmonic detection to that one expects from theory with the assumption of a Voigt lineshape. On the other hand, Figs. 1(a) and 1(b) show that at lower harmonics (the first and the second for example) the discrepancy is not as pronounced. This is seen clearly in Fig. 2 where the differences between the experimental signal and the theoretical signal that would be expected if the lineshape profile was a Voigt function are shown. Hence, it is seen that for harmonic detection at orders less than three the discrepancy between the Voigt signal and the actual experimental signal is less than approximately ten percent; on the other hand, with detection orders greater than three this discrepancy is greater than ten percent. In addition, in agreement with predictions, the differences are greater in the wings than near the line center.

It is known that the Voigt line shape function is only approximately valid. Simple arguments can illustrate this. For example, the Voigt function is a convolution of Gaussian and Lorentzian components. The Lorentzian results from the impact approximation, namely that the duration of intermolecular collision is assumed to be infinitesimally short. Clearly then the impact approximation, and therefore the Voigt lineshape function, overestimates the contributions in the wings. One, therefore, expects there to be a difference between the experimentally observed signal, and the one calculated using the Voigt profile, as indeed there is. Furthermore, the discrepancy is more obvious with higher harmonic detection.

There are basic scientific as well as practical reasons for obtaining accurate information of the wing structure of radiative transitions. The fact that the deviation of the wing structure from the Lorentzian line shape function is a consequence of the break down of the impact approximation means that the wing structure contains information about intermolecular collision dynamics. In any experiment where one measures the total signal that results form the presence of several overlapping lines, the wing structure clearly becomes of central importance. Examples of such experiments range from the SAGE III experiment, which is a part of the NASA Mission to Planet Earth Program, to astrophysical applications where stellar conditions are deduced from optical spectroscopy, to accurate determination of experimental parameters such as density, temperature and pressure in many scientific experiments as well as industrial processes.

The results shown in Fig. 1 also indicate that one can obtain N independent values of the collision broadening cross-section from an Nth harmonic detection experiment. It can be shown that there are, in general, N+1 turning points in an Nth harmonic detection measurement. If these turning point are labeled (see Fig. 1) $\lambda_{-j, N}$, $\lambda_{-(j+1), N}$ ...., it is seen that there are N independent wavelength intervals between the turning points that can be measured from one Nth harmonic detection experiment. Furthermore, these intervals depend upon the collision cross section (in addition to depending on the magnitudes the modulation indices, the relative phase difference between these modulations and, of course, upon the detection harmonic). Hence, since every
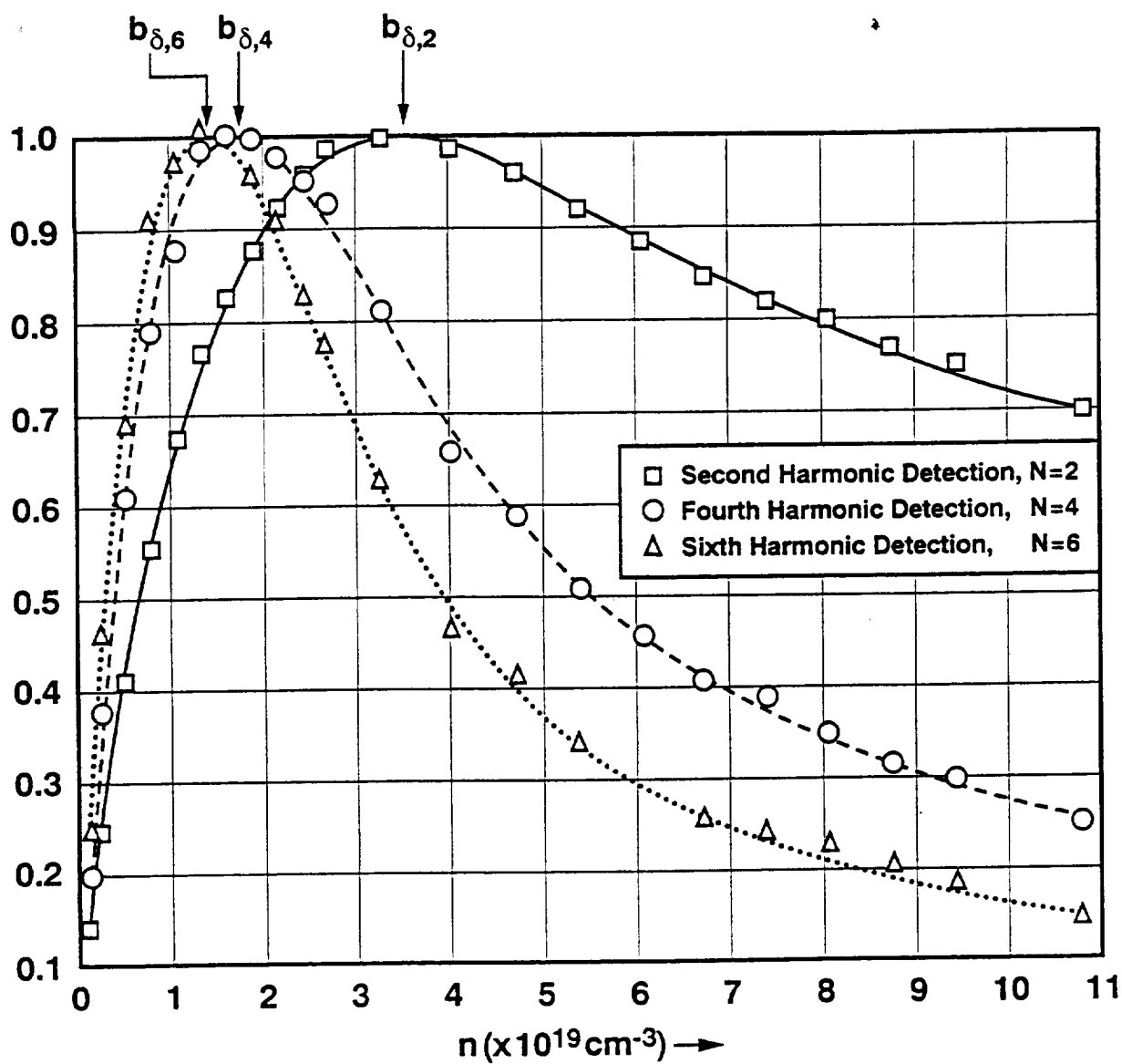
Fig. 3.　Dependence of signal magnitude on density for various harmonic detection orders

other parameter is measured, one effectively obtains N independent values of the collision cross-section.

We used this technique to measure the collision cross-section of rovibronic lines of the Oxygen A band. For this purpose, the wavelength and amplitude modulation indices were measured, together with the relative phase shift between them. The experimental signal could then be reproduced, assuming a Voigt line shape function, and the appropriate collision cross section was measured. For example, we see from Fig.1 that this measured cross-section is 1.7×10^{-15} cm^2 for the RQ (13, 14) line.

3(b)   Sensitive measurements of density, temperature and velocity fluctuations

We have shown [4] that the dependence of the signal magnitude on density depends strongly on the detection harmonic order used. To a first approximation one obtains a linear increase in the signal magnitude with density, for small densities in the regime corresponding to the Doppler broadened regime, for all harmonic detection orders. When the density increases above a characteristic density $n_{\delta,N}$, the signal magnitude falls approximately as n^{-N}. This region is the corresponding collision broadened regime and delineated from the Doppler broadened regime by $n_{\delta,N}$, a density which depends strongly on the detection harmonic order. This characteristic of the signal in the collision broadened region leads to the fact that the sensitivity of the signal to density fluctuations generally increases with N. This is illustrated in Fig. 3. The practical application of this behavior are clear: One may use a detection harmonic order greater than the commonly used second to measure smaller fluctuations in density.

The characteristic of a higher harmonic detection signal, mentioned above, is actually more general. For instance, assuming that the lineshape is a Voigt function, one can show that the behavior of the signal magnitude, in the collision broadened regime, varies approximately as b^{-N},

where b is the usual collision-broadening parameter given by $\quad b = \dfrac{n\sigma_{coll}v}{2\overline{\Delta v}} = \dfrac{\Delta v_{coll}}{2\overline{\Delta v_D}} = \dfrac{\delta v_o}{\overline{\Delta v_D}}$.

The consequence of this is that the sensitivity of the measurement to density fluctuations (at fixed temperature), or to the measurement of temperature fluctuations (at fixed density), as well as to simultaneous fluctuations of both the temperature and density, is generally larger with higher harmonic detection [4].

3(c)   Resolution of overlapping lines

We have also shown that wavelength modulation with harmonic detection leads to an increased wavelength resolution. In particular, nearly overlapping lines may be better resolved using higher harmonic detection than lower ones. The results shown in Fig. 4 illustrate this. These results are to be expected in light of the fact that wavelength modulation with harmonic detection gives signals that are derivative like and any features that are present as the result of overlapping lines are exhibited with greater contrast at higher derivatives than at lower ones. In effect this same characteristic of higher harmonic detection signals is one that results in an increased resolution of the wing structure of the absorption lines.

EXPERIMENTAL RESULTS

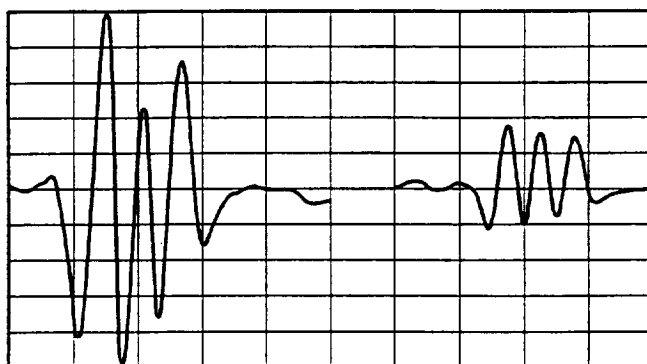## Pressure broadening in RR(17,17), RQ(15,16) and RR(21,21), RQ(19,20) lines
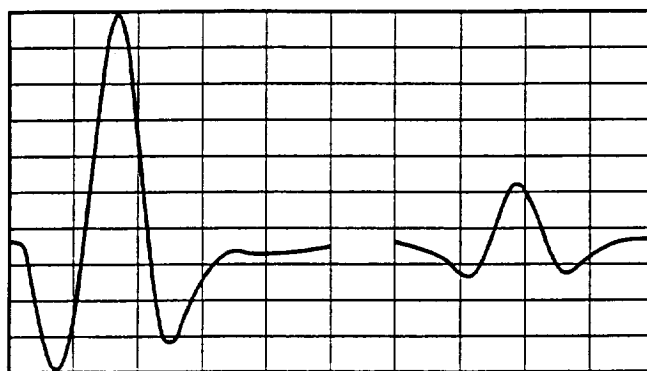
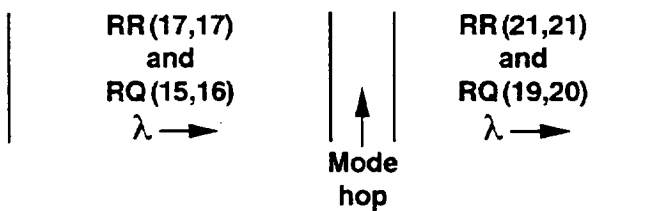**(a)**

$N=2$, $(m/m_0)=1.44$
Pressure=74.5 torr

(b)

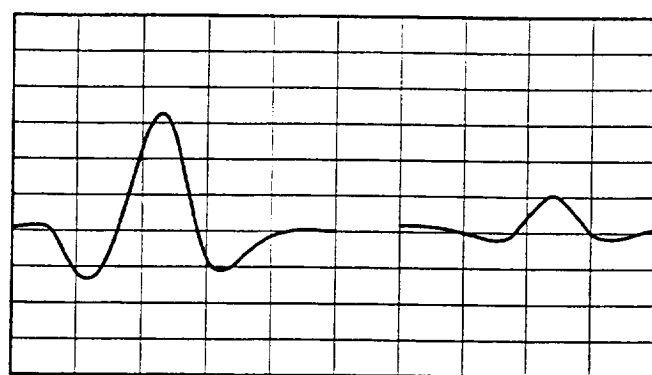$N=4$, $(m/m_0)=1.44$
Pressure=74.5 torr
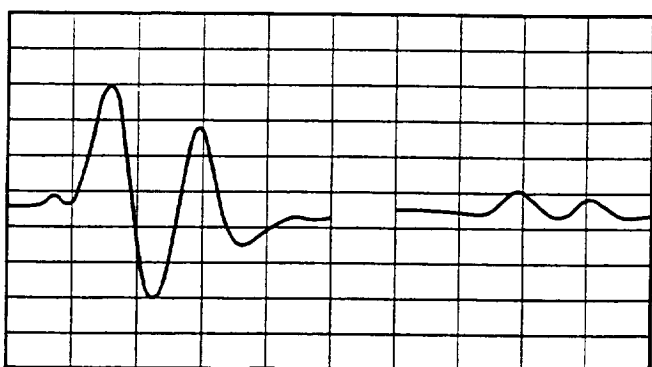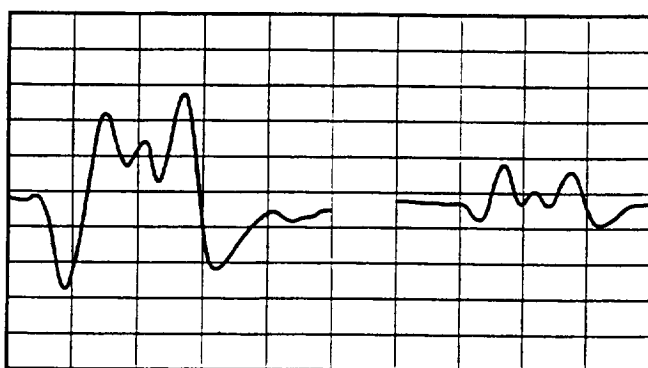
(c)

$N=6$, $(m/m_0)=1.44$
Pressure=74.5 torr

RR(17,17)
and
RQ(15,16)
$\lambda \longrightarrow$

RR(21,21)
and
RQ(19,20)
$\lambda \longrightarrow$

Mode
hop

(d)

N=2, (m/m$_0$)=1.44
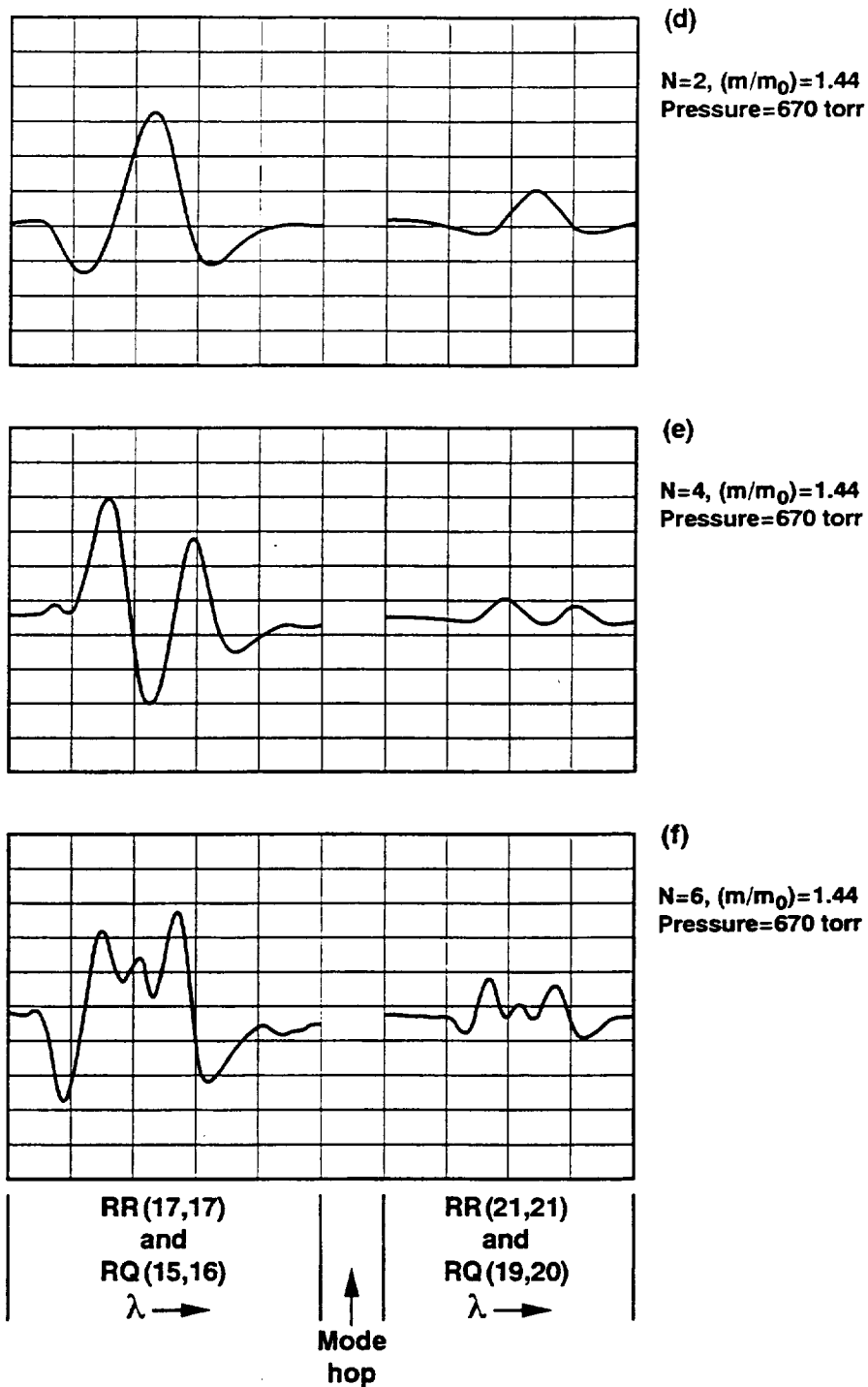Pressure=670 torr

(e)

N=4, (m/m$_0$)=1.44
Pressure=670 torr

(f)

N=6, (m/m$_0$)=1.44
Pressure=670 torr

RR(17,17)
and
RQ(15,16)
λ →

Mode
hop

RR(21,21)
and
RQ(19,20)
λ →

Fig. 4.   Resolution of lines by higher harmonic detection

(d)

N=2, (m/m_0)=1.44
Pressure=670 torr

(e)

N=4, (m/m_0)=1.44
Pressure=670 torr

(f)

N=6, (m/m_0)=1.44
Pressure=670 torr

RR(17,17)
and
RQ(15,16)
$\lambda \longrightarrow$

RR(21,21)
and
RQ(19,20)
$\lambda \longrightarrow$

Mode
hop
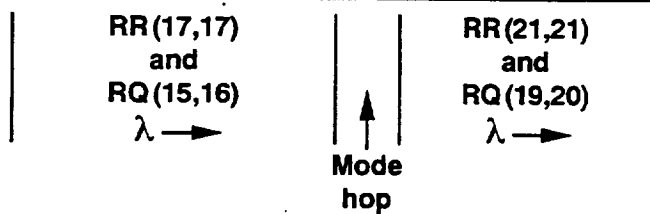
Fig. 4.   Resolution of lines by higher harmonic detection

ACKNOWLEDGMENTS

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